IN-SITU OBSERVATIONS OF HIGH TEMPERATURE SURFACE PROCESSES ON α-ALUMINA BULK CRYSTALS

Z. L. WANG* AND J. BENTLEY
Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376
* and Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN, 37996-2200.

ABSTRACT

Reflection electron microscopy (REM) was applied to image in-situ the dynamic changes of atomic-height steps on the surfaces of α-alumina bulk crystals heated to high temperatures. Atomic diffusion, desorption and adsorption processes on cleaved α-alumina (012) surfaces were directly observed at temperatures of 1470 to 1670 K. The surface started to show visible structural changes at 1470-1520 K. The main surface process appears to be atomic desorption, which creates large, flat vacancy-type terraces on the surface.

INTRODUCTION

Structures of bulk crystal surfaces can be imaged directly using glancing incidence high-energy electrons in a conventional transmission electron microscope (TEM) [1-4]. This technique is reflection electron microscopy (REM) and has been employed to image processes on semiconductor surfaces during in-situ heating experiments [5]. The REM technique can be combined with reflection electron energy-loss spectroscopy (REELS) to analyze local surface chemical compositions and related electronic structures [6]. Studying the behaviour of surfaces at high temperatures is of great importance for understanding the properties of ceramics and associated surface-gas reactions. Atomic processes occurring on bulk ceramic surfaces at temperatures of 1570 - 1670 K can be recorded by REM with relatively high resolution, because REM is especially sensitive to atomic-height steps.

A cleaved α-alumina crystal was mounted in a Gatan model 628 single-tilt heating holder in such a way that the single tilt of the holder effectively performed the two required tilts of the specimen to achieve the correct azimuth for the incident beam and reflection angle with respect to the optic axis. Video recordings of the dynamic surface processes occurring at high temperatures were made with the use of a Gatan model 622 intensified camera. The REM images shown here were obtained from unprocessed single frames of the video tapes. The REM experiments were performed in a Philips EM400T TEM equipped with a field emission gun (FEG) and operated at 100 kV.

At high temperatures, the image contrast was degraded by thermal diffuse scattering (TDS); the vibrations of surface and bulk atoms produce a strong background of diffuse scattering in the diffraction pattern and greatly reduce the resonance-Bragg reflections of electrons from the surface. However, acceptable images could still be obtained under certain diffraction conditions. In REM, the foreshortening effect distorts the surface image in the direction parallel to the beam, so that a circular surface step appears as a narrow elliptical shape.

TRANSITION TEMPERATURE OF α-ALUMINA (012) SURFACE

Cleaved surfaces of α-alumina (012) exhibit atomic flatness with steps of height about 5 Å, determined by reference to a screw (or near screw) dislocation with a presumed Burgers vector of $\mathbf{b} = (1/3)\langle 012\rangle$ (see Fig. 1). The surface processes stimulated by heating were imaged from room temperature (RT) up to 1670 K. Figure 2 shows a series of REM surface images of the same area heated to different temperatures. The surface appeared stable at temperatures below 1470 K and there was no obvious structural change. The surface steps started to move and some roughness began to develop at 1470 K. After being heated for about

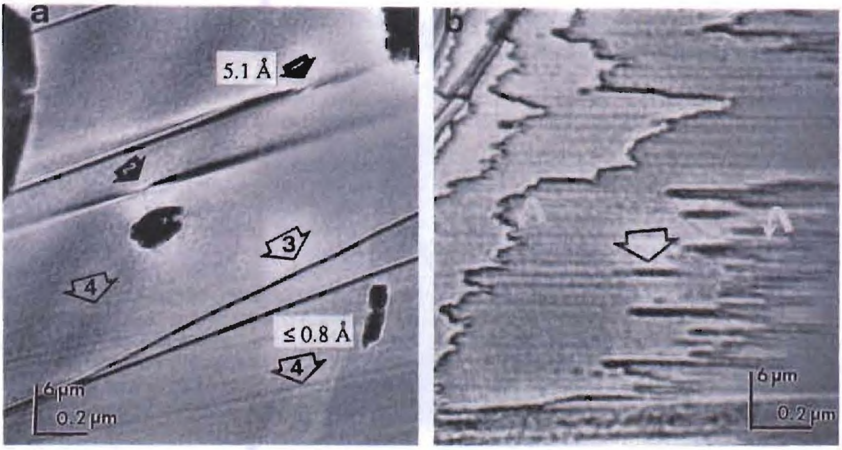

Fig. 1 REM images of an α-alumina (012) surface at 300 K showing (a) atomic-height surface steps and (b) vacancy-type terraces. Steps of heights less than about 0.8 Å can be resolved.

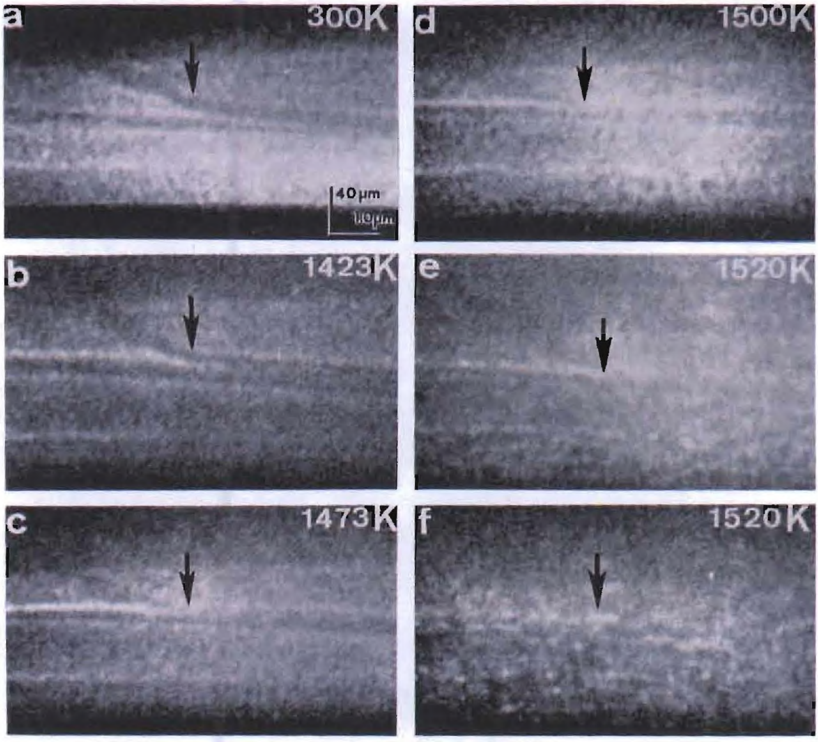

Fig. 2 REM surface images of the same area taken at different temperatures showing the effect of heating.

1 min at 1520 K, the whole surface was restructured and showed rough contrast as seen in Fig. 2f. These rough structures are the result of heat-induced surface desorption. The surface structure transition temperature is thus in the range 1470 to 1520 K.

As previously reported for α-Al_2O_3 (011) and (012) surfaces at RT [3,4], different contrast effects can be produced on regions with different atomic terminations by the radiation damage of the electron beam. The damage causes desorption of oxygen ions from surface domains initially terminated with oxygen and results in dark-rough contrast. The domains initially terminated with aluminum ions are stable and appear in bright contrast. Thus the "catalytic" effects of the incident electron beam could speed up surface desorption processes. However, it was found experimentally that the contrast observed in Fig. 2f appeared not only in the regions continuously illuminated with the beam but also in other areas not exposed to the beam. Therefore, the results shown in Fig. 2 are attributed solely to the effects of heating.

IN-SITU SURFACE DYNAMIC PROCESSES

Under the stimulation of heating at 1670 K, various surface processes can be generated. A series of REM images taken 15 s apart is shown in Fig. 3. The narrow ellipses are approximately circular surface steps if the foreshortening effect in the beam direction is considered. The directions of ledge movement are indicated for corresponding steps at different stages. The observed dynamic surface processes are the expansion of surface vacancy-type terraces (in dark contrast), which are one step-height lower than the areas with bright contrast. The vacancy-type terraces 1 and 2 are growing at a speed of 0.06 µm/s. The expansion of these terraces indicates that atomic desorption occurs at the ledges. Simultaneously with this desorption, surface diffusion can also be identified, as indicated with the arrowhead 3; the surface vacancy-type terrace fills up as time proceeds. This process is evidence of the presence of atomic diffusion from other surface areas and of surface adsorption.

A series of REM images, taken 20 seconds apart, of the same surface area at 1670 K is shown in Fig. 4. The vacancy-type terrace 1 in Fig. 4b is growing faster (0.09 µm/s) than terraces 2 and 3 (0.05 µm/s). The whole surface is being consumed by the darker contrast areas and shows fewer steps as time passes (Fig. 4d). Some second stage diffusion takes place inside

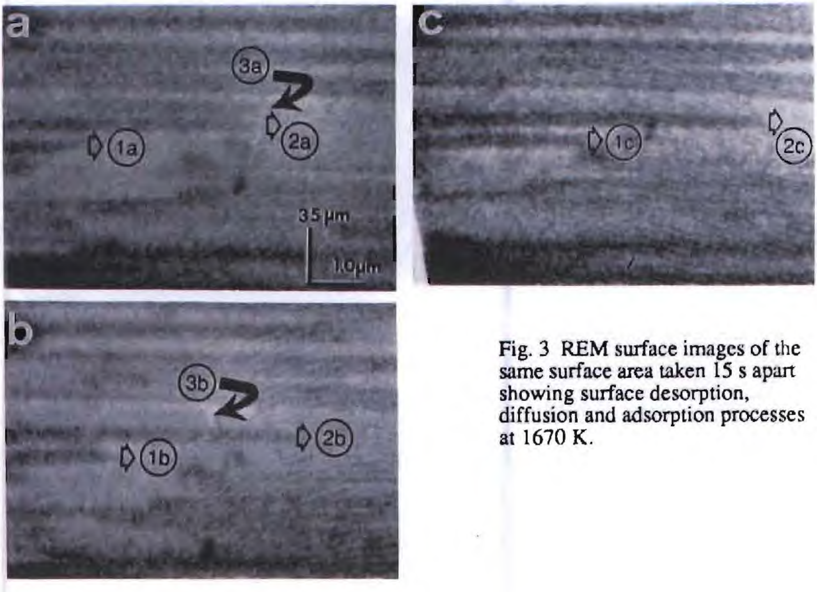

Fig. 3 REM surface images of the same surface area taken 15 s apart showing surface desorption, diffusion and adsorption processes at 1670 K.

the dark contrast areas, as indicated at arrowheads 7 and 8 in Fig. 4e and 4f; the vacancy-type terrace at arrowhead 9 starts to disappear. This observation is interpreted as indicating that some atoms are being transported from other areas to "fill up" this vacancy-type terrace. This result is expected thermodynamically as the surface approaches thermal equilibrium. However, there is actually no equilibrium surface structure if desorption continues.

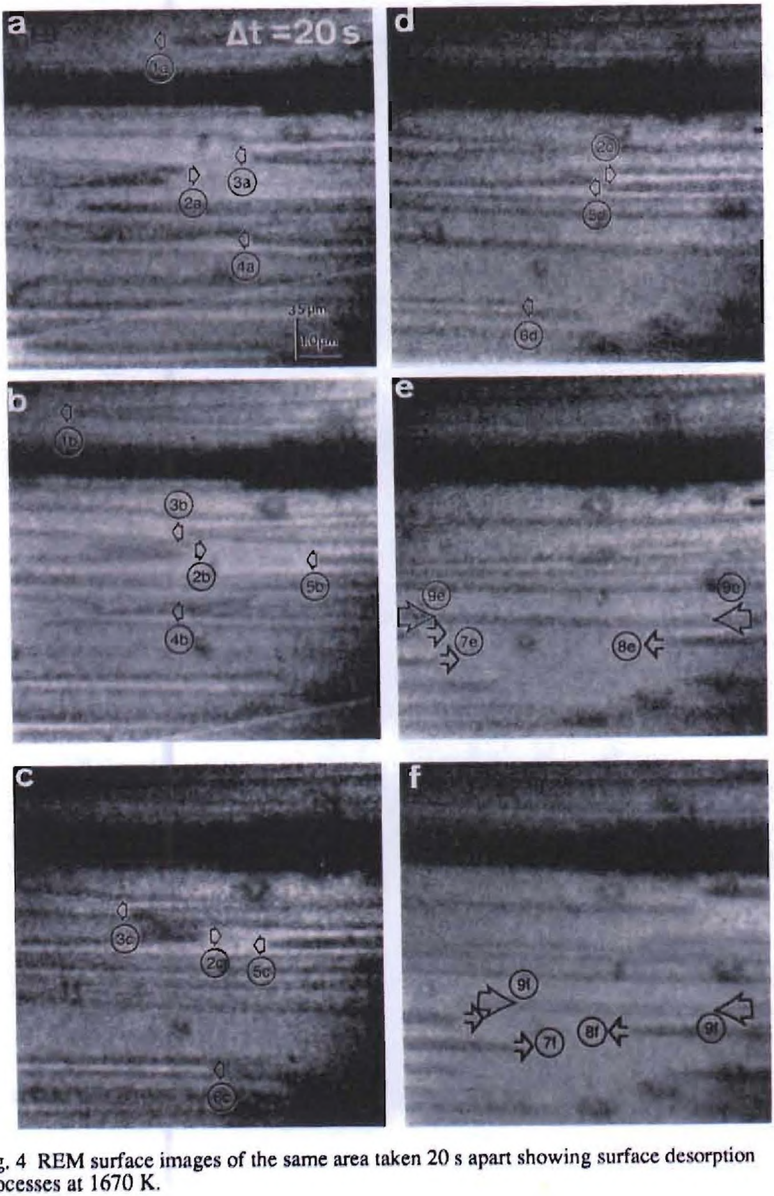

Fig. 4 REM surface images of the same area taken 20 s apart showing surface desorption processes at 1670 K.

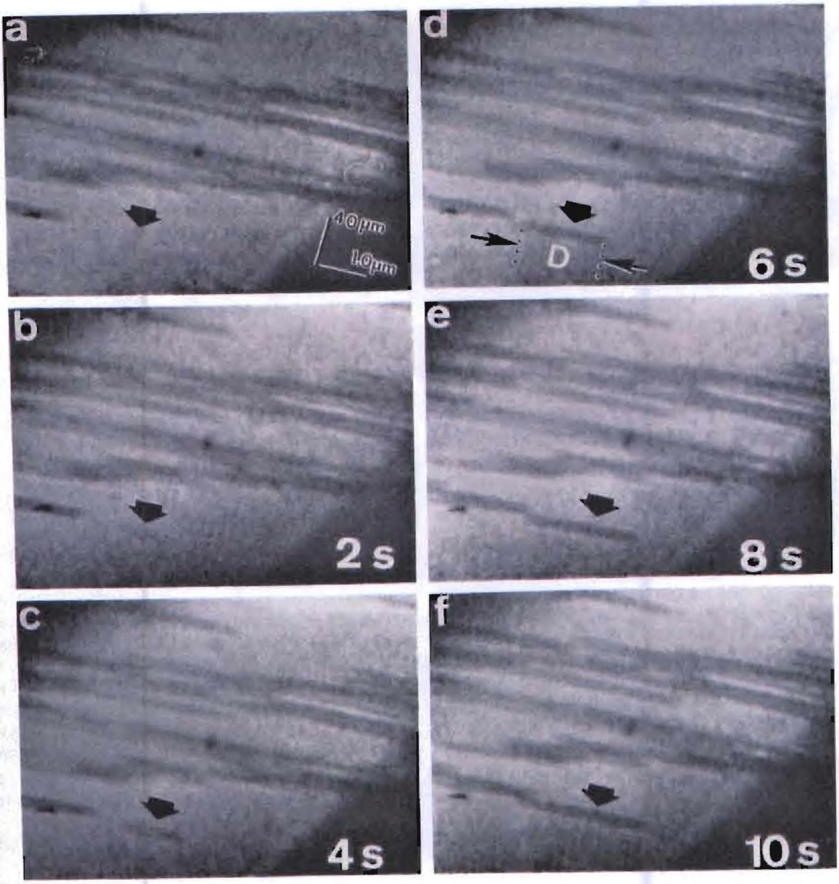

Fig. 5 REM surface images of the same area taken about 2 s apart at 1670 K showing the process of creating a new surface vacancy-type terrace, as indicated with an arrowhead.

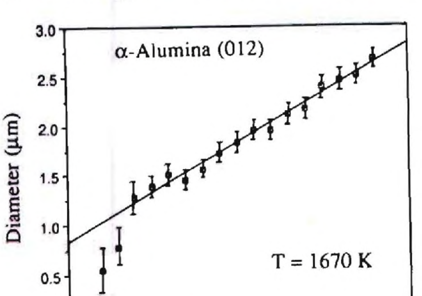

Fig. 6 The diameter of the newly created vacancy-type terrace arrowed in Fig. 5 as a function of time.

Besides the observed surface processes shown in Figs. 3 and 4, heating can also result in the nucleation of surface vacancy-type terraces. This process appears to start from surface areas with defects, as arrowed in Fig. 5a. The newly-created vacancy-type terrace grew fairly quickly at first when its diameter (D) was less than about 1.3 μm. After being heated for more than two seconds (Fig. 5b - 5f are at 2 s intervals), the growth rate dD/dt tends to be a constant (dD/dt = 0.2 μm/s in Fig. 6). The high initial growth rate may be because the atoms located close to a defect are most easily desorbed due to a lower binding energy, resulting in the nucleation of a new surface vacancy-type terrace. The inaccuracy of measuring D at the beginning makes it difficult to estimate its enhanced growth rate. After D is larger than about 1 μm, the influence of the original defect is negligible, and the desorption rate is determined mainly by the properties of the ledge around the vacancy terrace. If the vacancy terrace is considered as a circular loop, the atomic desorption rate dN/dt can be approximately written as

$$\frac{dN}{dt} \approx \frac{\pi}{2} D \frac{dD}{dt}\, s\, n_0 \exp\left(-\frac{E_s}{k_B T}\right), \qquad (1)$$

where n_0 is the density of the atoms per unit volume, s is the height of the ledge and E_s is the activation energy for sublimation. Since dD/dt is almost a constant, according to the results shown in Fig. 6, dN/dt increases linearly with the increase of D. Therefore, the atomic desorption rate is proportional to the terrace circumference if D > 1.3 μm.

SUMMARY AND CONCLUSIONS

Reflection electron microscopy (REM) can be applied to image in-situ the dynamic processes of atomic-height steps on the surfaces of α-alumina bulk crystals heated to high temperatures. Atomic level diffusion, desorption and adsorption processes on cleaved α-alumina (01$\bar{2}$) surfaces were directly imaged at temperatures of 1470-1670 K in a conventional transmission electron microscope. The temperature range above which the surface started to show visible structural changes was found to be 1470-1520 K. It is suggested that a vacancy-type terrace is most easily nucleated at a defect site. The atomic desorption rate is proportional to the circumference of the vacancy-type terrace if its diameter is larger than about 1.3 μm. The resolution and contrast of REM images can be significantly improved with a FEG; it is feasible to resolve steps with heights less than about 0.8 Å with a FEG, because REM images are dominated by phase contrast [7].

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